INVESTIGATION OF HUNGARIAN SULFIDE ORES OF VARIOUS ORIGIN BY MEANS OF ACTIVATION ANALYSIS

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Received: 15 May 1977

SUMMARY

It can be stated on the whole that the standard deviation of the results of measurements around the average varies according to samples and elements. The accuracy of activation measurements equals in general that of the traditional analytical methods or even surpasses it in certain cases. In case of some elements of ore minerals we can state that the demands (concerning sensitivity, accuracy, serial feasibility, economy etc.) determining the choice of analytical methods and the value of the obtainable informations *underline the advantages of the neutron activation method*, e. g. in case of Se, Ag, As, Sb, Co, La.

Part of the traditional methods requires in the case of the above mentioned elements more intricate sample preparatory, wet chemical (eventually separational) processes and assures the same or even less reproducibility (wet chemical analysis, spectrophotometry, atomic absorption), or *provides not so many informations* (e. g. spectroscopy, mass – spectrometry, X-ray fluorescence analysis). We may note that our analyses concerning the elements mentioned above are comparable with earlier analyses and in some a good conformity can be found.

We hope for further possibilites in extending the number of measurable elements especially concerning elements furnishing isotopes of shorter half-life (e. g. Ga, In, Mo, Re, Mn, Cl) as well as lanthanides (these latter as obtained from skarnic concentrates).

Applying epithermic activation the determination of e. g. Ni, Th and U becomes possible, further on the sensitivity and accuracy of Cd determination can be significantly increased.

Studies of this kind are going on, their results as well as interpretation of data will be dealt with in a later paper.

Introduction

Neutron activation analysis enables a sensitive and precise determination of many elements in geological samples too. Analysis of many siliceous rocks [Modern trends ..., 1969; Allen – Haskin – Anderson – Müller, 1970; Brunfelt – Steinnes (Eds), 1971), meteorites, lunar samples (Brunfelt – Steinnes, 1971; Levinson, 1970; Brunfelt – Steinnes – Sundroll, 1977] have been carried out, and as a result earlier Clark-distributions of some elements had to be corrected.

The extension of irradiations to the epithermic domain increased the number of determinable elements and in some cases also the sensitivity and accuracy of the determinations too (Steinnes, 1971; Randa, 1976).

The activation analysis turned to be a useful method of investigation of standard reference-materials, so of the study of minerals and rocks, first of all in the domain of trace concentrations, (Gordon – Randle – Goles – Corliss – Beeson – Oxley, 1968; Cojocaru – Ispas, 1971; Brätter – Lausch – Rösick, 1975).

Relatively few attention has been paid so far to a nondestructive multicomponent analysis of sulfide ores. At first Lamb et al. (1966) carried out such measurements by means of a Ge(Li) semiconductor detector, in the course of which determinations of elements furnishing isotopes of small and medium half-life have been made. Later on, Steinnes et al. (1973) and Randa (1976) carried out instrumental analyses of sulfides and ore concentrates.

The paper presents the results of nondestructive analyses carried out by means of neutron activation on "averaged" ores, monomineral fractions from the mineralization of Recsk serving for standardization purposes as well as on a few other ores of diffent composition, genesis and place of occurrence. The investigations have included first of all trace and secondary elements being important geochemically and practically, such as: Cu, Zn, Se, Ag, As, Cd, Sb, Co, Au, Sc, La.

Samples and standards

Samples under investigation can be grouped as follows:

I. Polimetallic and monomineral fractions of the mineralization of Recsk used as reference material (according to the numbering of Table II.):

1. Dispersed pyrite ore
2. Dispersed chalcopyrite-pyrite ore
3. Chalcopyrite-pyrite skarne-ore
4. Sphalerite-pyrite skarne-ore
5. Sphalerite-pyrite "metasomatic" ore
6. Polimetallic "metasomatic" ore
7. Sphalerite
8. Pyrite
9. Galenite, sphalerite, chalcopyrite
10. Chalcopyrite, pyrite

II. Other samples coming from the mineralization of Recsk:

11. Chalcopyrite, pyrite from skarn
12. Chalcopyrite, pyrite from skarn
18. Pyrite from skarn
20. Enargite
21. Luzonite
24. Skarnic vein
25. Skarnic vein
26. Skarnic vein

III. Monomineralic fractions from various Hungarian finding places:

13. Chalcopyrite, pyrite, Gyöngyösoroszi
14. Chalcopyrite, pyrite, Rudabánya
15. Chalcopyrite, pyrite, Nagylápafő
19. Sphalerite, Nagylápafő
22. Galenite, Gyöngyösoroszi (flotationed ore)
23. Galenite, Nagybörzsöny.

IV. Samples from foreign finding places:

16. Chalcopyrite, pyrite, Texas Gulf, Canada
17. Chalcopyrite, pyrite, Vrly Brjag, Bulgaria.

For the quantitative determination solutions of p. a. or spectroscopic purity of the components were used.

Pretreatment of samples and standards for the irradiation

Quantities of the samples of about 100 mg (measured with analitical precision) were packed into small polyethylene boxes. In order to assure uniform measuring geometry, 100 μl quantities of the standard solution (measured by means of micropipette) were taken separately into similar boxes, then dropped into silica gel and dryed out using an infra lamp.

According to earlier observations the boxes contained the elements sought for under the limit of detectability, so that before the measurements a repacking became unnecessary.

Irradiation, measurements

Irradiation of the samples took place in the Training Reactor of the Technical University Budapest.

For Cu-determinations the pneumatic irradiation system of the reactor ($\varphi_{\text{term}} = 2{,}8 \times 10^{11} n\ \text{cm}^{-2} s^{-1}$), for the production of isotopes of longer half-life one of the vertical irradiation channels) $\varphi_{\text{term}} = 2{,}4 \times 10^{11} n\ \text{cm}^{-2} s^{-1}$) were used.

In case of irradiation by the pneumatic system times of 20 min, for channel irradiation times of 24 hours were applied.

Simultaneously with the samples and standards also copper flux-monitors were irradiated.

Measurements have taken place in case of the short time irradiations after 2 – 3 hours, while for the long time irradiations delays of 5 days and 3 months were applied.

For the measurements a semiconductor detector "Princeton Gamma Technique Ge (Li) and joint KFKI made 4096 channel analyser was used. The resolution of the detector was 2.2 keV related to the 1332 keV peak of ^{60}Co.

Table I.

Nuclear parameters of the elements investigated and conditions of measurements

Element	Isotope used for the determination	Abundance (%) *	Cross section (barn)*	Nuclear reaction	Gamma-energy of the „analytic peak" (keV)**	Half-life*	Irradiation time (hours)	Cooling time (days)	Measuring time (sec)
Sc	^{45}Sc	100	13	^{45}Sc (n, γ) ^{46}Sc	889,4; 1120,3	83,9 days	24	90	2000
Co	^{59}Co	100	17	^{59}Co (n, γ) ^{60}Co	1173,1; 1332,4	5,24 years	24	90	2000
Cu	^{63}Cu	69,1	4,5	^{63}Cu (n, γ) ^{64}Cu	511 ; 1345,5	12,8 hours	20	0,1	200
Zn	^{64}Zn	48,49	0,82	^{64}Zn (n, γ) ^{65}Zn	1115,4	234 days	24	90	2000
As	^{75}As	100	4,30	^{75}As (n, γ) ^{76}As	559,2	26,3 hours	24	5	2000
Se	^{74}Se	0,87	30	^{74}Se (n, γ) ^{75}Se	264,6; 279,6	121 days	24	90	2000
Ag	^{109}Ag	48,65	4,2	^{109}Ag (n, γ) ^{110m}Ag	675,8; 937,2	253 days	24	90	2000
Cd	^{114}Cd	28,86	0,30	^{114}Cd (n, γ) ^{115}Cd	492,5; 527,7	2,3 days	24	5	200
Sb	^{121}Sb	57,25	6,2	^{121}Sb (n, γ) ^{122}Sb	564,0	2,75 days	24	5	2000
	^{123}Sb	42,75	3,4	^{123}Sb (n, γ) ^{124}Sb	62,6; 1690,7	60,9 days		90	
La	^{139}La	99,911	8,8	^{139}La (n, γ) ^{140}La	159,954	40,27 hours	24	5	2000
Au	^{197}Au	100	98,8	^{197}Au (n, γ) ^{198}Au	411,8	2,70 days	24	5	2000

* *E. Bujdosó, I. Fehér, G. Kardos:* Activation and Decay Tables of Radioisotopes. Akadémiai Kiadó, 1973.

** *F. Adams, R. Dams:* A compilation of precisely determined gamma-transition energies of radionuclides produced by reactor irradiation. J. Radioanal. Chem. 3 (1969) 99—125.

For both samples and for both positions two parallel irradiations have been carried out, so we obtained for the elements furnishing radioisotopes of short half-life at least 2, for those with longer half-life 2 or 4 parallel data. (Several usable peaks, – e. g. in case of La, Cu, or several radioisotopes of various halflives such as ^{122}Sb, ^{124}Sb – even accordingly more). Irradiational, cooling and measurement parameters as well as the most important physical constants of the radioisotopes used are contained in Table I.

Computation of the results of measurements

Spectra recorded on punch tape have been analysed by the computer RAZDAN – 3 of the Computer Center of the University. Besides the complete list of spectra the programm used contains the following data of higher importance:

- the place of the peak (the serial number of the channel),
- the value of gamma-energy belonging to the given channel number,
- the area of the peak,
- the statistical error of the area of the peak,
- the statistical error in percent of the peak area.

In addition the programm determines in parts of the spectrum chosen in advance the volume of peak area still usable – in the given domain (in case of a given background) – for quantitative measurements or for detection of an isotope (Currie-levels, C u r r i e, 1968). So we were able to give the lower concentration limit of the determinability also in cases, when the method was not sufficiently sensitive for a quantitative evaluation.

Given the knowledge of peak areas we computed corrections for uniform irradiation – cooling – and measuring time intervals, for uniform neutron flux, geometric measuring positions as well as for standards and for the samples investigated. Calculations were carried out on the desktop calculator, type: Hewlett – Packard 9810 of the Institute of Mineralogy of the University.

Gamma-spectra of some mineral fractions (pyrite, chalcopyrite, sphalerite, galenite) are shown on Figs. 1, 2, 3 and 4.

Summary of the results of measurements

Results of measurements are assembled in Table 2. Mean concentrations are shown as well as single standard deviations computed on the basis of parallel measurements are given expressed in the same units as the mean concentrations. When needed also detection limits computed on the base of Currie levels are given.

Copper: Measuring accuracy – besides simplicity and quickness – is comparable to that of conventional (electrogravimetric, photometric) methods, depending on concentration and

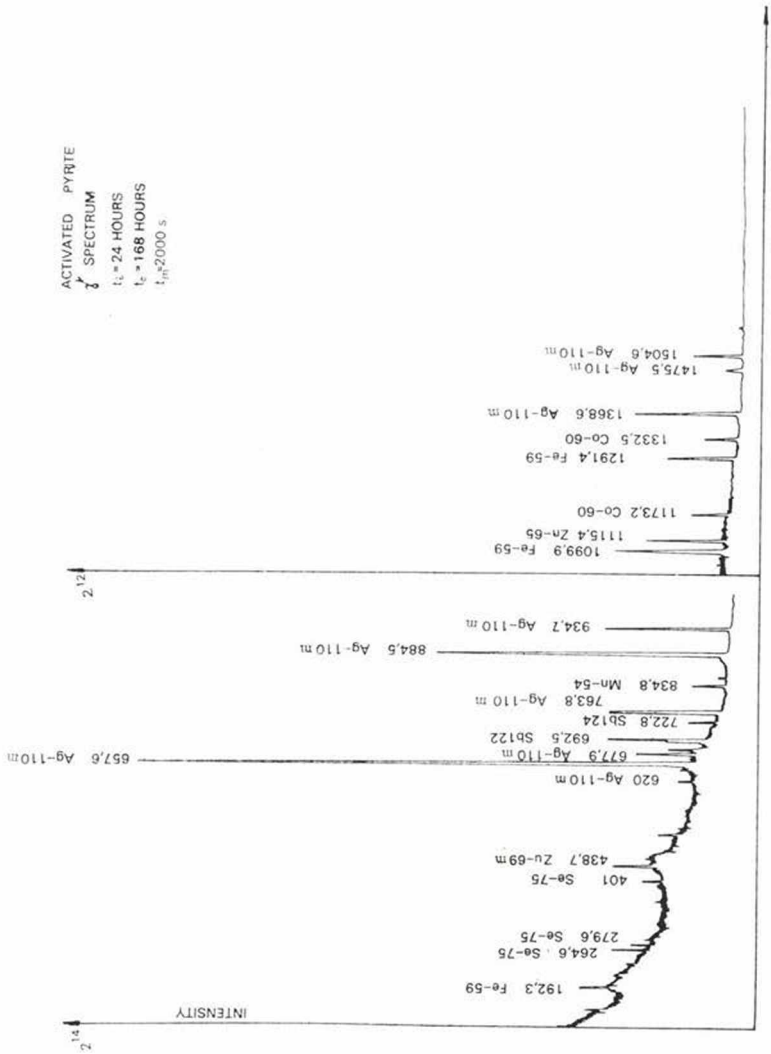

Fig. 1. Gamma-spectrum of activated pyrite (irradiation time: 24 hours, cooling time: 168 hours, measuring time: 2000 sec)

matrix material: 0.2% (relative) (29.28% Cu) – 15% (0.02% Cu). In case of multicomponent serial measurements the method can be proposed as a method for the determination of macro respectively accesoric component.

Zinc: Lower limit of quantitative evaluability (for the measuring parameters) is about 0.008%. Measuring accuracy: 0.7% (65.03% Zn) – 17% (0.123% Zn). As regards applicability of the method the conditions are the same as given above with copper.

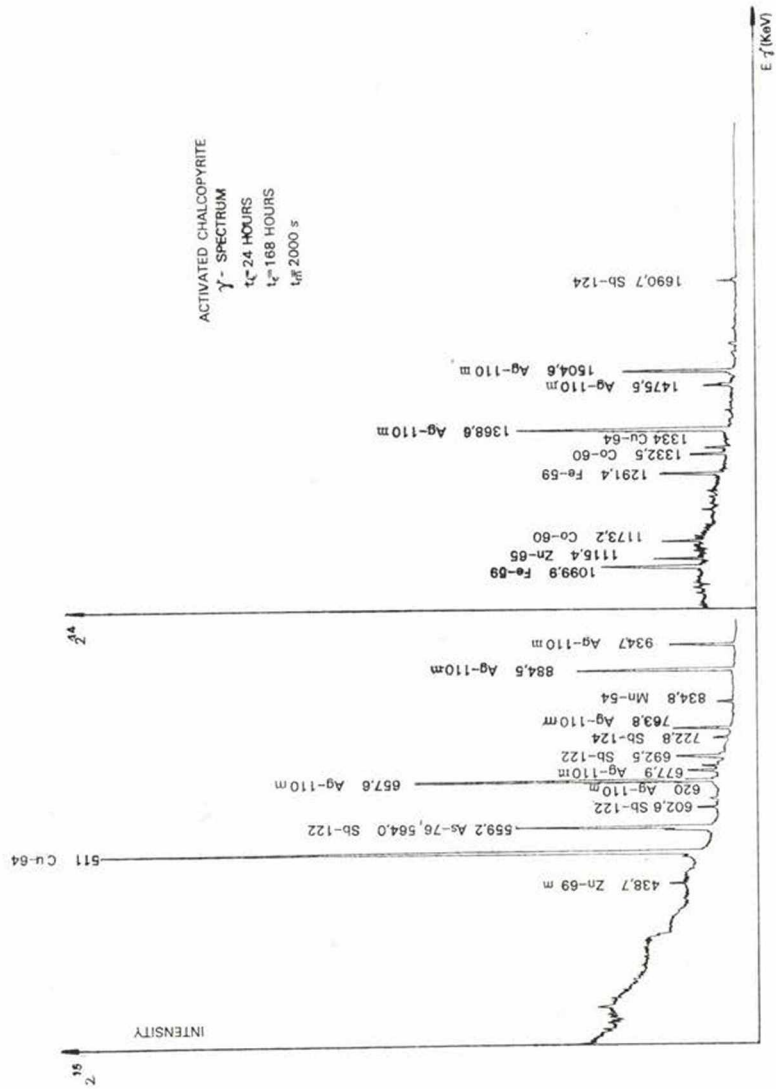

Fig. 2. Gamma-spectrum of activated chalcopyrite (irradiation time: 24 hours, cooling time: 168 hours, measuring time: 2000 sec)

Selenium: Measuring accuracy: 2% (3397 ppm Se) −21% (14 ppm Se). Selenium is one of the elements measurable with high sensitivity and accuracy (when needed the parameter can be significantly increased by changing of measuring conditions). It is recommended for quick and nondestructive trace analyses.

Silver: Lower limit of quantitative measureability is 4 ppm. By means of increase of irradiation, measuring and cooling

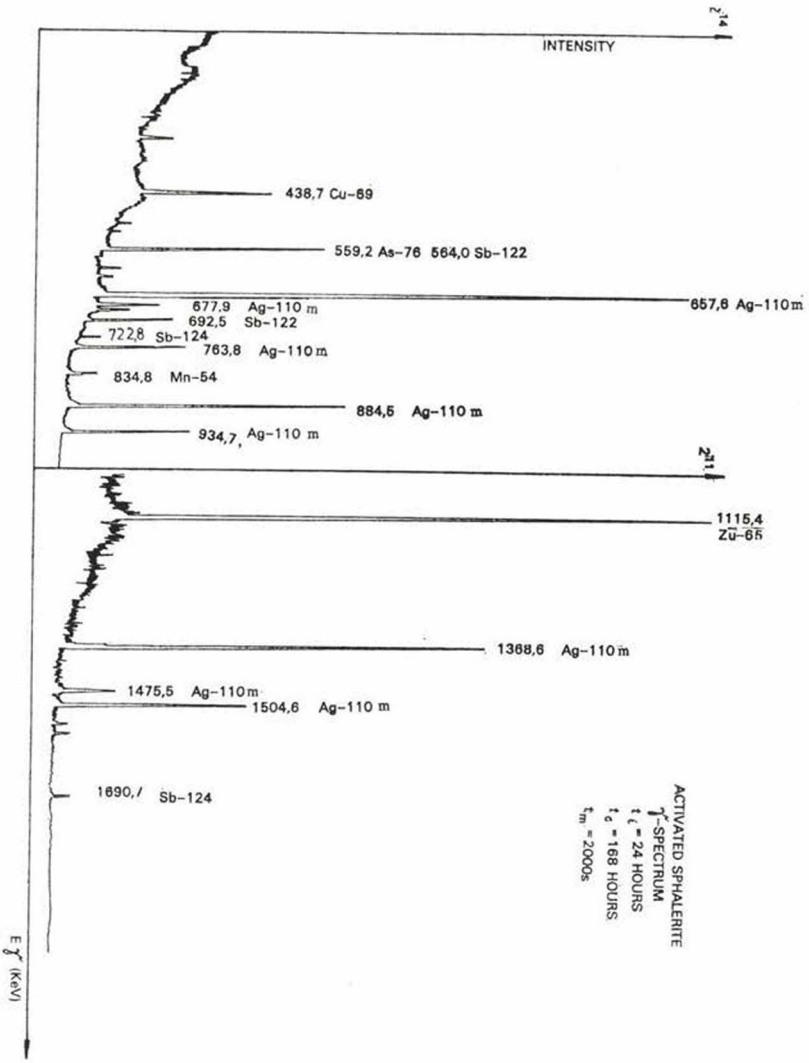

Fig. 3. Gamma spectrum of activated sphalerite (irradiation time: 24 hours, cooling time: 168 hours, measuring time: 2000 sec)

times, sensitivity and accuracy can be increased. Measuring accuracy: 6.5% (368 ppm Ag) −40% (4.4 ppm Ag).

Arsenic: It is an element with precise determinability. In case of nondestructive measurement with the presence of antimony of higher quantity application of correction is needed. Measuring accuracy: 0.6% (3616 ppm As) −11,8% (17 ppm As).

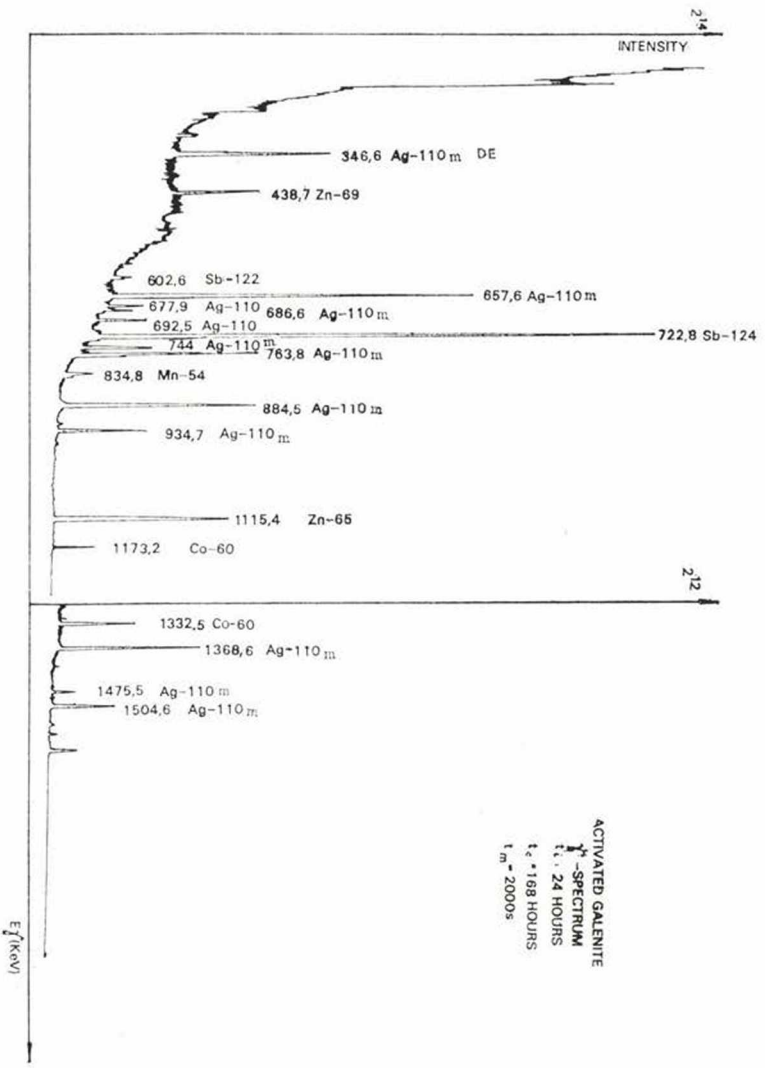

Fig. 4. Gamma-spectrum of activated galenite (irradiation time: 24 hours, cooling time: 168 hours, measuring time: 2000 sec)

Cadmium: On account of significant background interference it can be measured only with moderate accuracy and sensitivity. Lower limit of valuability is about 15 ppm.
Measuring accuracy: 0.9% (6363 ppm Cd) −48% (23 ppm Cd).

Antimony: It can be measured without destruction sensitively and precisely. In case of the parameters applied the measuring accuracy is: 0.8% (5857 ppm Sb) −25% (0,8 ppm Sb).

Cobalt: It can be measured simply, precisely and sensitively from any matrix material.
Measuring accuracy: 3.3% (264 ppm Co) —45% (3 ppm Co), limit of detectability about 1 ppm.

Gold: It can be measured with extremely high sensitivity and accuracy. Its determination is not influenced by other elements. Measuring accuracy: 8.6% (837 ppm Au) —20% (0.1 ppm Au).

Scandium: Owing to its favourable nuclear parameters its determination can be made from any mineral or rock sensitively and precisely. Limit of detectability is about 2 ppm Sc.
Measuring accuracy: 5% (21 ppm Sc) —20% (5.5 ppm Sc).

Lanthanum: Remarks made for scandium are valid here too. Lanthanides are — with a few exceptions — well measurable by

Summary of results

		Cu %	Zn %	Se ppm	Ag ppm
1 1739/71	Disseminated pyrite ore	0,59 ± 0,09	< 0,008	23 ± 6	< 5
2 1742/71	Disserminated chalcopyrite-pyrite ore	1,35 ± 0,19	0,09 ± 0,01	26 ± 10	5 ± 2
3 1740/71	Chalcopyrite-pyrite skarne-ore	3,19 ± 0,26	0,023 ± 0,004	155 ± 21	∅ 5
4 1741/71	Sphalerite-pyrite skarne-ore	0,26 ± 0,01	6,94 ± 0,08	742 ± 37	36 ± 8
5 1743/71	Sphalerite-pyrite „metasomatic" ore	0,45 ± 0,01	6,11 ± 0,12	55 ± 11	< 5
6 1744/71	Polymetallic „metasomatic" ore	6,60 ± 0,11	9,86 ± 0,20	271 ± 31	38 ± 12
7 2634/1	ZnS	0,43 ± 0,03	65,03 ± 0,40	127 ± g2	84 ± 22
8 2634/3	FeS_2	0,26 ± 0,02	0,46 ± 0,03	325 ± 29	< 5
9 2634/6	PbS < ZnS < $CuFeS_2$	4,32 ± 0,12	9,98 ± 0,12	3397 ± 68	368 ± 24
10 2634/22	$CuFeS_2$ < FeS_2	29,28 ± 0,04	0,25 ± 0,02	981 ± 40	34 ± 6
11	Recsk RM — 35, $CuFeS_2$ < FeS_2	11,85 ± 0,03	0,001	575 ± 131	25 η ± 3
12	Recsk RM — 32, $CuFeS_2$ < FeS_2	11,34 ± 0,30	0,001	899 ± 115	69 ± 5

means of neutron activation method. Measurability limit: about 4 ppm.
Measuring accuracy: 6% (245 ppm La) – 20% (5 ppm La).

In case of samples 20. and 21. (enargite, respectively luzonite) the background activity of As and Sb – being present as main components – is so high that determination of Cu and Cd is not possible, while the quantity of As is not comparable with the As content of the standard. Thus, their place has been left blank in the table.

Acknowledgements

We are indebted to Dr. T. Zelenka (National Ore-and Mineral Mines for having made available part of the samples.

Table II.

of measurements

As ppm	Cd ppm	Sb ppm	Co ppm	Au ppm	Sc ppm	La ppm
626±10	<15	4±1	14±3	0,2±0,02	14±1	17±5
97±4 97±4	23±11	9±2	30±4	0,3±0,05	12±0,6	99±6
3616±21	20±8	8±2	23±5	0,6±0,1	8,5±0,5	245±15
868±26	<15	26±3	20±3	1,1±0,1	5,5±1,1	43±3
273±18	533±18	7±2,5	42±2	<0,1	21±1	95±4
1784±15	583±67	17±5	264±12	<0,1	<2	23±1
331±29	6363±61	245±11	3±1	0,1±0,02	<2	<4
1184±32	<15	8±2	16±2	0,6±0,06	<2	<4
39±3	915±36	24±4	10±2	<0,1	<2	<4
598±55	182±26	36±3	42±4	2,0±0,1	<2	5±1
17±2	57±6	0,8±0,2	70±7	4,7±0,1	<2	<4
90±3	144±13	3,9±0,2	116±1	1,7±0,1	<2	<4

(conti

		Cu %	Zn %	Se ppm	Ag ppm
13	Gyöngyösoroszi $CuFeS_2 < FeS_2$	16,06 ± 0,06	0,03 ± 0,001	1669 ± 53	394 ± 21
14	Rudabánya, $CuFeS_2 < FeS_2$	13,56 ± 0,05	0,001	14 ± 3	35 ± 3
15	Nagylápafő, $CuFeS_2 < FeS_2$	5,07 ± 0,03	0,30 ± 0,01	81 ± 5	63 ± 5
16	Texas Gulf, Canada $CuFeS_2 < FeS_2$	12,19 ± 0,05	0,56 ± 0,02	845 ± 12	71 ± 8
17	Vrly Brjag-Burgas, Bulgaria $CuFeS_2 < FeS_2$	7,86 ± 0,04	0,002 ± 0,001	77 ± 8	9 ± 1
18	Recsk RM – 35, FeS_2	0,53 ± 0,01	0,001	336	74 ± 12
19	Nagylápafő, ZnS	0,14 ± 0,02	62,33 ± 0,53	185 ± 14	251 ± 24
20	Recsk, enargite		0,10 ± 0,01	231 ± 8	586 ± 15
21	Recsk, luzonite		0,08 ± 0,01	1469 ± 70	42 ± 6
22	Gyöngyösoroszi PbS(flotated ore)	0,12 ± 0,01	0,16 ± 0,01	32 ± 4	9 ± 1
23	Nagybörzsöny, PbS	0,22 ± 0,02	0,04 ± 0,01	16 ± 2	227 ± 8
24	Recsk, RM – 35	0,02 ± 0,003	0,45 ± 0,08	< 10	< 5
25	Recsk, RM – 27 952 – 953 m	0,20 ± 0,01	0,28 ± 0,05	115 ± 10	28 ± 10
26	Recsk, RM – 30 649 – 649,5 m	0,02 ± 0,003	1,21 ± 0,06	< 10	93 ± 18

Table II.

nued)

As ppm	Cd ppm	Sb ppm	Co ppm	Au ppm	Sc ppm	La ppm
119 ± 4	365 ± 32	103 ± 2	9 ± 2	0,5 ± 0,1	< 2	< 4
355 ± 13	171 ± 22	18 ± 1	68 ± 3	0,5 ± 0,1	< 2	< 4
103 ± 9	144 ± 21	6,3 ± 0,5	68 ± 3	0,3 ± 0,1	< 2	< 4
21 ± 2	204 ± 23	4,5 ± 0,3	14 ± 2	0,2 ± 0,05	< 2	< 4
69 ± 2	15	2,5 ± 0,2	192 ± 8	0,3 ± 0,03	< 2	< 4
47 ± 4	2466 ± 370	156 ± 5	1	0,1 ± 0,025	< 2	< 4
		4670 ± 40	12 ± 1	540 ± 43	< 2	< 4
		5857 ± 45	12 ± 1	837 ± 72	< 2	< 4
246 ± 29	138 ± 12	2 ± 0,5	8 ± 1	0,4 ± 0,1	< 2	< 4
3 ± 0,3	233 ± 34	1,7 ± 0,2	39 ± 6	0,2 ± 0,05	< 2	± 4
4,4 ± 1,8	59 ± 6	5 ± 0,5	8 ± 4	0,05 ± 0,02	10,8 ± 1,4	28 ± 2
5 ± 2	48 ± 5	5 ± 0,4	18 ± 5	0,4 ± 0,04	13,2 ± 1,4	17 ± 1
139 ± 4	173 ± 13	6,3 ± 0,4	8 ± 3	0,03 ± 0,04	32 ± 1	771 ± 8

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